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(54) NEGATIVE TONER FOR DEVELOPING ELECTROSTATIC CHARGE IMAGE AND METHOD FOR MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a toner which is used for the method of nonmagnetic single-component development and which stably gives high-quality image characteristics from the initial stage to the life end and to provide a method for manufacturing the toner.
SOLUTION: In the negative toner for developing an electrostatic charge image comprising at least a binder resin and a coloring agent, the binder resin is a polyester resin having each specified weight average molecular weight Mw, ratio Mw/Mn to the number average molecular weight Mn and peaks P1, P2 of the molecular weight in the molecular weight distribution by GPC, the amount of the high molecular weight component and the acid value of the resin. The method for manufacturing the toner is carried out by preliminarily preparing a pigment dispersion master batch by using a copolymer polyester of 2-mol adduct of bisphenol-A propylene oxide and fumaric acid or maleic acid, then mixing the batch with the binder resin and other toner materials, melting and kneading, and dispersing the coloring agent in the toner.

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CLAIMS

[Claim(s)]
[Claim 1] In the toner which consists of binding resin and a coloring agent at least, this binding resin is polyester resin. Mw/Mn is 20-50. GPC molecular weight distribution -- setting -- weight average molecular weight Mw -- a ratio with 70000 or more and number average molecular weight Mn -- There is at least one peak value P1 in the location of molecular weight 3000-20000. The negative electrification nature toner for electrostatic-charge image development which the peak to which a with a molecular weight of 150000 or more component exceeds one third of the height of P1 to 150000 or more molecular weight 10 to 30% does not exist, but is characterized by the resin acid number being 5 or less mgKOH/g.
[Claim 2] In the manufacture approach of the toner which consists of binding resin and a coloring agent at least It is copolymerized polyester with the two mol addition product of bisphenol A propylene oxide, a fumaric acid, or a maleic acid. To the acid number 7 - 15 mgKOH/g, and a with a weight average molecular weight of 50000 or less thing The toner manufacture approach which builds beforehand the pigment-content powder masterbatch by which distributed mixing of the above-mentioned coloring agent was carried out, carries out melting kneading of this masterbatch after mixing with binding resin and other toner ingredients further, and is characterized by making a coloring agent distribute in a toner.
[Claim 3] The toner according to claim 1 which it is copolymerized polyester with the two mol addition product of bisphenol A propylene oxide, a fumaric acid, or a maleic acid, and the pigment-content powder masterbatch by which distributed mixing of the above-mentioned coloring agent was carried out is built [toner] beforehand, and melting kneading of this masterbatch is further carried out [toner] after mixing with binding resin and other toner ingredients, and makes the acid number 7 - 15 mgKOH/g, and a with a weight average molecular weight of 50000 or less thing come to distribute a coloring agent in a toner in the toner which consists of binding resin and a coloring agent at least.
[Claim 4] The toner manufacture approach according to claim 1 to 3 or toner which contains one or more sorts chosen from salicylic-acid metallic compounds, a boron complex, or annular phenol system oligomer 0.5 to 10% of the weight as an electrification control agent contained in a toner.
[Claim 5] The toner manufacture approach according to claim 1 to 4 and toner which are used for the nonmagnetic 1 component developing-negatives method with which the coat of the toner is carried out by the blade on a development sleeve, and the development of an electrostatic-charge image is presented.
[Claim 6] The Magenta toner manufacture approach according to claim 1 to 5 and Magenta toner which contain at least one sort chosen from the group of the C.I. pigment red 122, the C.I. pigment red 238, the C.I. pigment red 146, and the C.I. pigment red 57:1 in 1 - 5% of the weight of the range as a coloring agent.
[Claim 7] The Magenta toner manufacture approach according to claim 1 to 5 and Magenta toner which contain the C.I. pigment red 122 and the C.I. pigment red 238 in 1 - 4% of the weight of the range as a coloring agent, respectively.
[Claim 8] The cyanogen toner manufacture approach according to claim 1 to 5 and cyanogen toner

which contain a copper-phthalocyanine pigment one to 5% of the weight as a coloring agent.
[Claim 9] The yellow toner manufacture approach according to claim 1 to 5 and yellow toner which contain at least one sort chosen from the group of the C.I. pigment yellow 17, the C.I. pigment yellow 74, and the C.I. pigment yellow 180 in 1 - 5% of the weight of the range as a coloring agent.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacture approach of of the nonmagnetic monocomponent toner and the toner which are used for a xerography, an electrostatic recording method, and magnetic recording.
[0002]
[Description of the Prior Art] Although the approach of a large number indicated by a U.S. Pat. No. 2,297,691 specification, JP,42-23910,B, JP,43-24748,B, etc. as a xerography is learned conventionally Generally use the photoconductivity matter and an electric latent image is formed on a photo conductor with various means. Subsequently, develop this latent image using a toner and a direct and indirect means is used if needed. After imprinting a toner image to imprint material, such as paper, it is established with heating, pressurization, heating and pressurization, or a solvent steam, and an imprint object is not obtained, the toner which remained without imprinting on a photo conductor is cleaned by various approaches, and an above-mentioned process is repeated.
[0003] The miniaturization of equipment and improvement in the speed are advancing as the image formation equipment using the electrophotographic technology like a copying machine or a laser beam printer spreads widely in recent years. In such, the 1 component development system in which simplification of a developing machine and a miniaturization are possible has spread rather than the conventional 2 component development system. Although the system of a ************ 1 component magnetism toner has been well used in the magnetic substance into a toner, in order to form a full color image, the system which uses color-enhancing good nonmagnetic monocomponent toner is spreading through this 1 component development system quickly with the spread of the latest color printers.
[0004]
[Problem(s) to be Solved by the Invention] After an image is developed by the latent image with the spread of the latest color printers, in order for a transfer paper not to imprint for every color but to form full color development, the image of each color is formed in a middle imprint object like an imprint belt or an imprint drum, and the method by which a package imprint is carried out after that has spread. In the conventional system, although a transfer paper imprints after a toner is developed by the photo conductor etc., and fixed by fixing system like a heating roller, by adoption of a middle imprint system, the imprint process increased and the problem that the yield of a waste toner increases has arisen.
[0005] Moreover, also coming to diversify the environment used and corresponding to a large temperature-and-humidity environment with the spread of small color printers, is called for. Although nonmagnetic 1 component development is the most desirable development system as a system of a small color printer, it is difficult to be stabilized and to acquire the image property of high quality from the first stage to the LIFE end, corresponding to a large temperature-and-humidity environment in the case of nonmagnetic 1 component development. Especially, under low-humidity/temperature and high-humidity/temperature, in front of the initial image and toner piece immediately after cartridge opening, a fogging may arise, nonuniformity may arise in a poor image, or spilling may occur in the circumference

of an alphabetic character, or when consumption increases unusually, fixing offset may arise, or it may become causes, such as a paper jam in the time of double-sided printing, from distortion of a transfer paper.

[0006] Moreover, although it was a quality technical problem with the image concentration of the poor section important in the case of the conventional monochrome image, in the case of a color picture, importance is attached to the repeatability of the concentration of the halftone image section called a halftone. The repeatability of the concentration of this halftone image section is difficult in nonmagnetic 1 component development. Thus, in addition to the stability of the image concentration in the poor section, the stability of the concentration of the halftone image section is also demanded further.

[0007] Thus, in the small printer which forms a full color image, although nonmagnetic 1 component development is the most desirable development system, the toner for acquiring the image property of high quality to which the problem that it is difficult to be stabilized and to acquire the image property of high quality from the first stage to the LIFE end is satisfied is called for.

[0008] The purpose of this invention was made in view of the above-mentioned situation, is used for the nonmagnetic 1 component development approach, and tends to offer the toner which is stabilized and acquires the image property of high quality from the first stage to the LIFE end, and its manufacture approach.

[0009]

[Means for Solving the Problem and its Function] this invention persons found out ****** which changes greatly with the dispersibility of the pigment with which the dispersibility to the inside of the toner of each component added to a toner affects the imprint property of a toner, and image concentration, and serves as especially a coloring agent that the concentration of the halftone image section is stabilized, and when the development property of a halftone part also chooses an electrification control agent, as a result of inquiring wholeheartedly.

[0010] Consequently, the binding resin in this invention is polyester resin, and this polyester resin sets to GPC (gel permeation chromatography) molecular weight distribution. Mw/Mn is 20-50. weight average molecular weight Mw -- a ratio with 70000 or more and number average molecular weight Mn -- There is at least one peak value P1 in the location of molecular weight 3000-20000. The peak to which a with a molecular weight of 150000 or more component exceeds one third of the height of P1 to 150000 or more molecular weight 10 to 30% does not exist. While the negative electrification nature toner for electrostatic-charge image development with which the acid number of the resin to contain comes out, and is characterized by 5 or less mgKOH/g of a certain thing had the outstanding imprint property, the image concentration of the poor section to halftone was also high, and it found out that it was stable.

[0011] Since the toner itself is the particle size which is several micrometers, it is necessary to distribute in a toner the coloring agent used for a toner with a still finer particle size. Moreover, the dispersibility of color enhancement of a coloring agent is as high as a good thing, and the distributed property of a coloring agent affects an electrification property pan at a development property. In distributing a coloring agent in a toner, the viscosity of resin and the polarity used as the principal component of a toner influence greatly. Conventionally, as resin used for the toner for full color, from the problem of the color mixture nature at the time of piling up a color, weight average molecular weight was small, and resin with low melt viscosity was used, and the thing beyond it was used before and after resin also with a high polarity, i.e., acid-number 10 mgKOH/g. What makes the acid number low rarely was for using for a forward electrification nature toner.

[0012] When this invention persons examined the stability of the image concentration of a halftone part, the one where the acid number is lower found out that it was good for the stability of the image concentration of a halftone part using resin with high weight average molecular weight.

[0013] Moreover, the thing which is called a masterbatch and which made the pigment distribute in resin beforehand is mixed with resin or the main ingredients, melting kneading is carried out, and the approach of raising pigment-content powder is learned. Also in the ingredient kind of the resin using this masterbatch, or a polarity, it is influential, and the concentration of halftone becomes high by using copolymerized polyester with the two mol addition product of bisphenol A propylene oxide, fumaric acid, or maleic acid which is the acid number 7 - 15 mgKOH/g, and 50000 or less mean molecular weight.

[0014] Furthermore, as toner binding resin, are polyester resin and it sets to GPC molecular weight distribution. Mw/Mn is 20-50. weight average molecular weight Mw -- a ratio with 70000 or more and number average molecular weight -- There is at least one peak value P1 in the location of molecular weight 3000-20000. The peak to which a with a molecular weight of 150000 or more component exceeds one third of the height of P1 to 150000 or more molecular weight 10 to 30% does not exist. While using the resin whose acid number of binding resin is 5 or less mgKOH/g improves the image concentration of a halftone part further in combination with this masterbatch, it excels also in a durable property. Furthermore, it controls that a toner disperses from a development sleeve, and the printer which forms an image, and the dirt by toner scattering inside a copying machine are mitigated.

[0015] Moreover, the environmental capability of the quality of printing stabilizes the toner of this invention by containing one or more sorts chosen from salicylic-acid metallic compounds, a boron complex, or annular phenol system oligomer 0.5 to 10% of the weight as an electrification control agent contained to a toner particle.

[0016] Although especially a fogging and spilling tend to appear notably under a high-humidity environment and a damp environment, the toner of this invention shows a desirable property under high-humidity/temperature or low-humidity/temperature. This is considered for influencing a development property while the moisture content which is sticking to a toner front face adsorbs moderately.

[0017]

[Embodiment of the Invention] In the toner with which this invention has binding resin and a coloring agent at least Binding resin is polyester resin and this polyester resin sets to GPC molecular weight distribution. Mw/Mn is 20-50. weight average molecular weight Mw -- a ratio with 70000 or more and number average molecular weight -- There is at least one peak value P1 in the location of molecular weight 3000-20000. The peak to which a with a molecular weight of 150000 or more component exceeds one third of the height of P1 to 150000 or more molecular weight 10 to 30% does not exist, but the acid number of the resin to contain is the negative electrification nature toner for electrostatic-charge image development which comes out and is characterized by 5 or less mgKOH/g of a certain thing.

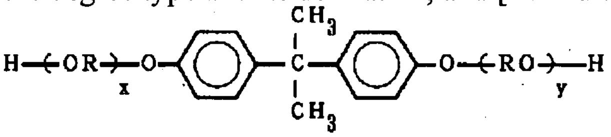
[0018] the GPC molecular weight distribution of the polyester resin in this invention -- setting -- weight average molecular weight Mw -- a ratio with 70000 or more and number average molecular weight -- Mw/Mn is 20-50 and it is that the peak to which there is at least one peak value P1 in the location of molecular weight 3000-20000, and a with a molecular weight of 150000 or more component exceeds one third of the height of P1 to 150000 or more molecular weight 10 to 30% does not exist.

[0019] Moreover, when P1 exceeds 20000, the melting property in low temperature comes to be bad inferior to low-temperature fixable one. In the molecular weight distribution in GPC weight average molecular weight Mw 70000 or more Mw/Mn is 20-50 and there is at least one peak value P1 in the location of molecular weight 3000-20000. a ratio with number average molecular weight -- It comes to have the outstanding fixing property, fully holding the offset nature at the time of an elevated temperature, when the peak to which a with a molecular weight of 150000 or more component exceeds one third of the height of P1 to 150000 or more molecular weight 10 to 30% does not exist. Moreover, when making it the peak to which a with a molecular weight of 150000 or more component exceeds one third of the height of P1 to 150000 or more molecular weight 10 to 30% not exist, the amount of amount of macromolecules should check fixable, and distribution of a coloring agent should be excelled.

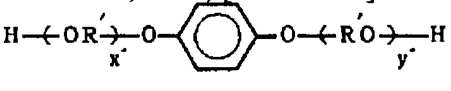
[0020] Furthermore, a GPC chart top peak does not exist in 150000 or more molecular weight, but molecular weight is missing from a macromolecule from low-molecular, and few [continuously] methods of intermediary **** are excellent in the endurance of a toner. this -- a GPC chart top -- large -- two peaks -- because the dispersibility of an ingredient is excellent is thought from intermediary **** -- having .

[0021] Moreover, although it is desirable that there is nothing as for a tetrahydrofuran (THF) insoluble element, even if there is, it is 1% or less of a resinous principle. if it exceeds 1%, the dispersibility of an ingredient will be resembled and it will have a bad influence.

[0022] The measuring method of the molecular weight distribution of the THF meltable component of a resin constituent is as follows.
[0023] First, the sample for the GPC measurement in the case of polyester resin is produced as follows. After putting in polyester resin into THF and leaving it for several hours, it mixes well enough until the coalescence object of polyester resin is lost, and puts for further 12 hours or more. It is made for the neglect time amount to the inside of THF to turn into 24 hours or more at this time. then, the thing which passed the sample processing filter (the pore size H-25-5 by TOSOH CORP. of 0.45-0.5 micrometers, for example, a my SHORI disk, germane Science Japan EKIKURO disk 25CR, etc. can be used) -- the sample of GPC -- it carries out. Polyester resin concentration is prepared so that a resinous principle may become in ml and 0.5-5mg /.
[0024] In the case of binding resin, the solid which evaporated toluene and was obtained is mixed with chloroform from the toluene extract of a toner, chloroform dispersion liquid are obtained, chloroform dispersion liquid are filtered, and it separates into chloroform insoluble solid content and the filtrate of a chloroform solution. Chloroform is evaporated from filtrate, a solid is mixed with THF, and the sample for GPC measurement is produced like the case of polyester resin.
[0025] The molecular weight and molecular weight distribution by GPC of the THF meltable component of polyester resin and the THF meltable component of binding resin are measured by the following approaches. In a 40-degree C heat chamber, a column is stabilized, as a solvent, about 100microl impregnation of a sink and the THF sample solution is carried out, and THF is measured at the rate of 1ml/m in the column in this temperature. In the molecular weight measurement of a sample, the molecular weight distribution which a sample has is computed from the relation of the opposite numeric value of a calibration curve and the number of counts which were created by several sorts of mono dispersion polystyrene standard samples. As a standard polyester sample for calibration-curve creation, the molecular weight by the TOSOH CORP. make or Showa Denko K.K. is 102-107, for example. It is appropriate to use the standard polystyrene sample of about at least six points using what is extent. RI (refractive index) detector is used for a detector. As a column, it is good to combine two or more commercial polystyrene gel columns.
[0026] The acid number of the polyester resin of this invention is 5 or less mgKOH/g. Since the acid number is small, environmental capability when a coloring agent is included becomes desirable. Concentration change may be caused, when the acid number exceeds 5 mgKOH/g and a large number are printed at low temperature and the time of damp.
[0027] The presentation of the polyester resin used for this invention is as follows.
[0028] As an alcoholic divalent component, they are the biphenol shown by ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol, 2, 3-butanediol, a diethylene glycol, triethylene glycol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 2-ethyl -1, 3-hexandiol, hydrogenation bisphenol A, or the degree type and its derivative, and [Formula 1].



(However, R is ethylene or a propylene radical among a formula, and x and y are zero or more integers, respectively, and the averages of x+y are 0-10)
Moreover, diols, [Formula 2] which are shown by the degree type



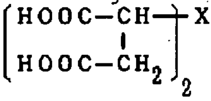
(However, R' expresses -CH2 CH2-, -CH2 and CH(CH3)-, or -CH2 and C(CH3)2- among a formula, and x' and y' are zero or more integers, respectively, and the averages of x'+y' are 0-10) etc. -- it is mentioned and these are independent -- or it is used by two or more sorts, mixing.
[0029] As a divalent acid component, for example Moreover, a phthalic acid, a terephthalic acid, an

ISOSO phthalic acid, Benzene dicarboxylic acid, the anhydride of those, or low-grade alkyl ester, such as phthalic anhydride; An amber acid, Alkyl dicarboxylic acid, its anhydride, or low-grade alkyl ester;n-dodecenyl succinic acids, such as an adipic acid, a sebacic acid, and an azelaic acid, Alkenyl succinic acids or alkyl succinic acids, such as n-dodecyl succinic acid, Or the anhydride or low-grade alkyl ester; dicarboxylic acid, such as partial saturation dicarboxylic acid, such as a fumaric acid, a maleic acid, a citraconic acid, and an itaconic acid, an anhydride of those, or low-grade alkyl ester;, and the derivative of those are mentioned.

[0030] Moreover, it is desirable when using together the alcoholic component more than trivalent [which is committed also as a bridge formation component] or the acid component more than trivalent raises endurance.

[0031] As an alcoholic component more than trivalent, for example A sorbitol, 1 and 2, 6-hexane triol, 1, 4-sorbitan, pentaerythritol, dipentaerythritol, Tripentaerythritol, 1 and 2, 4-butane triol, 1 and 2, 5-pentanetriol, glycerol, isobutane triol, and 2-methyl - 1, 2, 4-butane triol, trimethylolethane, trimethylol propane, 1 and 3, 5-trihydroxy benzene, etc. are mentioned, and these are independent -- or it is used by two or more sorts, mixing.

[0032] moreover, as a multiple-valued carboxylic-acid component more than trivalent [in this invention] For example, trimellitic acid, pyromellitic acid, 1,2,4-benzenetricarboxylic acid, 1, 2, 5-benzene tricarboxylic acid, 2 and 5, 7-naphthalene tricarboxylic acid, 1, 2, 4-naphthalene tricarboxylic acid, 1 and 2, 4-butane tricarboxylic acid, 1, 2, 5-hexane tricarboxylic acid, 1, a 3-dicarboxyl-2-methyl-2-methylene carboxy propane, Tetrapod (methylene carboxyl) methane, 1, 2 and 7, 8-octane tetracarboxylic acid, en pole trimer acids and these anhydrides, or low-grade alkyl ester; [Formula 3] shown by the degree type



$$\left[\begin{matrix}\mathrm{HOOC-CH}\\ |\\ \mathrm{HOOC-CH_2}\end{matrix}\right]_2 \mathrm{X}$$

(X expresses the with a carbon number of 30 or less alkylene group or alkenylene group which may have one or more with a carbon numbers of one or more side chains among ** and a formula) multiple-valued carboxylic acids, the derivatives of those, etc., such as these anhydrides and low-grade alkyl ester, such as tetracarboxylic acid, are mentioned, and these are independent -- or it is used by two or more sorts, mixing.

[0033] the blending ratio of coal of the alcoholic component used for this invention -- 40-60-mol% -- desirable -- the blending ratio of coal of a 45-55-mol % and acid component -- 60-40-mol% -- it is 55-45-mol% preferably. Moreover, as for the component of many ** more than trivalent, it is desirable that it is [1-60 mol] % in [all] a component.

[0034] Moreover, the toner of this invention may use other resin together in 20% of range. As a class of binding resin used together, for example Polystyrene; Polly p-KURORU styrene, The single polymer of styrene substitution products, such as polyvinyl toluene; A styrene-p-KURORU styrene copolymer, A styrene-vinyltoluene copolymer, a styrene-vinyl naphthalene copolymer, A styrene-acrylic ester copolymer, a styrene-methacrylic ester copolymer, A styrene-alpha-Krol methyl-methacrylate copolymer, a styrene acrylonitrile copolymer, A styrene-vinyl methyl ether copolymer, a styrene-vinyl ethyl ether copolymer, A styrene-vinyl methyl ketone copolymer, a styrene-butadiene copolymer, Styrene system copolymers, such as a styrene-isoprene copolymer and a styrene-acrylonitrile-indene copolymer; A polyvinyl chloride, Phenol resin, natural denaturation phenol resin, natural resin denaturation mallein resin, Acrylic resin, methacrylic resin, Pori acetic-acid vinyl, silicone resin, polyester resin, polyurethane, polyamide resin, furan resin, an epoxy resin, xylene resin, a polyvinyl butyral, terpene resin, cumarone indene resin, petroleum system resin, etc. are mentioned.

[0035] Moreover, the styrene resin over which the bridge was constructed may be used together. Especially, the system copolymer of styrene is desirable from the field [polyester resin] of compatibility.

[0036] As a comonomer to the styrene monomer of a styrene system copolymer For example, an acrylic acid, a methyl acrylate, an ethyl acrylate, butyl acrylate, Acrylic-acid dodecyl, acrylic-acid octyl, 2-ethylhexyl acrylate, Acrylic-acid phenyl, a methacrylic acid, a methyl methacrylate, ethyl methacrylate, The monocarboxylic acid which has double bonds, such as methacrylic-acid butyl, methacrylic-acid octyl, acrylonitrile, a methacrylonitrile, and acrylamide, or its substitution product; for example The dicarboxylic acid which has double bonds, such as a maleic acid, maleic-acid butyl, maleic-acid methyl, and maleic-acid dimethyl, or its substitution product; for example Vinyl ester, such as a vinyl chloride, vinyl acetate, and benzoic-acid vinyl; for example Ethylene system olefins, such as ethylene, a propylene, and a butylene; for example Vinyl ketones, such as a vinyl methyl ketone and a vinyl hexyl ketone for example, vinyl monomers, such as vinyl ether, such as vinyl methyl ether, vinyl ethyl ether, and vinyl isopropyl ether, are mentioned, and these are independent -- or two or more sorts can use it, mixing. the compound which mainly has the double bond in which two or more polymerizations are possible as a cross linking agent used here uses -- having -- for example, aromatic series divinyl compound [, such as a divinylbenzene and divinyl naphthalene,]; -- for example Ethylene glycol diacrylate, ethylene glycol dimethacrylate, Carboxylate which has two double bonds, such as 1,3-butanediol dimethacrylate; A divinyl aniline, the compound which has divinyl compound [, such as the divinyl ether, a divinyl sulfide, and divinyl sulfone,]; and three or more vinyl groups is mentioned, and these are independent -- or two or more sorts can use it, mixing.

[0037] The toner of this invention can use for copolymerized polyester with the acid number 7 - 15 mgKOH/g, 50000 or less mean molecular weight, the two mol addition product of bisphenol A propylene oxide and a fumaric acid, or a maleic acid the pigment-content powder masterbatch by which distributed mixing was carried out. Improvement in image concentration and improvement in halftone development nature can be aimed at by using for copolymerized polyester with the acid number 7 - 15 mgKOH/g, 50000 or less mean molecular weight, the two mol addition product of bisphenol A propylene oxide and a fumaric acid, or a maleic acid the pigment-content powder masterbatch by which distributed mixing was carried out.

[0038] A pigment dispersion surface has the well desirable toner manufacturing method which the pigment-content powder masterbatch by which distributed mixing was carried out in the coloring agent at copolymerized polyester with the acid number 7 - 15 mgKOH/g, 50000 or less mean molecular weight, the two mol addition product of bisphenol A propylene oxide and a fumaric acid, or a maleic acid was built [manufacturing method] beforehand, and melting kneading of this was further carried out [manufacturing method] after mixing with resin and other toner ingredients, and made the coloring agent distribute in a toner from the field of improvement in image concentration.

[0039] By the masterbatch, pigment-content powder becomes good, and it improves making concentration improve, and is **********. However, this invention persons found out that the image concentration of halftone improved further by using copolymerized polyester with the two mol addition product of bisphenol A propylene oxide, a fumaric acid, or a maleic acid as resin further. Although this reason is not clear, the resin used for the masterbatch presumed to be the property difference of a polyester monomer kind is 50000 or less or more 3000 weight average molecular weight in the molecular weight distribution in GPC, and, as for Mw/Mn, ten or less thing is used. Tg is a middle point method by DSC, and a 50-65-degree C thing is used. As for a hydroxyl value, the thing of 8-25 is used.

[0040] In these masterbatch manufactures, other additives are enough mixed with a Henschel mixer and a mixer like a ball mill if needed, and the approach of carrying out melting kneading of the obtained mixture using a heat kneading machine like a heating roller, a kneader, and an extruder or the approach of carrying out mixed kneading of the copolymerized polyester under a pigment-content powder solution, ordinary pressure, or pressurization is mentioned to copolymerized polyester and a coloring agent pan at them.

[0041] 20% - 55% of the content of the coloring agent in a masterbatch is desirable. At less than 20%, if there is little effectiveness of pigment-content powder and it exceeds 55%, manufacture with a heat kneading machine will become difficult.

[0042] Furthermore, it sets to the molecular weight distribution in GPC as this masterbatch and binding resin. Mw/Mn is 20-50. weight average molecular weight Mw -- a ratio with 70000 or more and number average molecular weight -- There is at least one peak value P1 in the location of molecular weight 3000-20000. The peak to which a with a molecular weight of 150000 or more component exceeds one third of the height of P1 to 150000 or more molecular weight 10 to 30% does not exist. While improving the image concentration of a halftone part further by making a toner contain the polyester resin whose acid number of the resin to contain is 5 or less mgKOH/g, it excels also in a durable property. Furthermore, it controls that a toner disperses from a development sleeve, and the printer which forms an image, and the dirt by toner scattering inside a copying machine are mitigated.

[0043] As a coloring agent used for this invention, it is possible to use the following.

[0044] As a black coloring agent, what was toned by mixed black in carbon black, aniline black, acetylene black, red ocher, an azo system color, the magnetic substance, or the below-mentioned yellow / below-mentioned Magenta / cyanogen coloring agent can be used.

[0045] although the furnace black manufactured by the channel black and the furnace method which were manufactured with the channel process is used in case carbon black is used as a black coloring agent -- the thing of the range of pH 2-10 -- desirable -- the thing of the range of pH 2-5 -- using -- ****. As first [an average of] particle size, the thing of the range of 20-50nm is used.

[0046] As the magnetic substance, there is a metallic oxide containing elements, such as iron, cobalt, nickel, copper, magnesium, manganese, aluminum, and silicon, etc. Especially, what uses iron oxides, such as a tri-iron tetraoxide and gamma-iron oxide, as a principal component is desirable. The BET specific surface area by the nitrogen adsorption process is desirable, the particle of these magnetic substance has good 2-30m2 / g, and its 3-28m2 / g are especially good. Furthermore, the magnetic particle of 5-7 has desirable Mohs hardness. As a configuration of a magnetic particle, although there is the shape of eight face pieces, six face pieces, a globular form, a needle, and a scale etc., what has few anisotropies, such as eight face pieces, six face pieces, a globular form, and an indeterminate form, is desirable. It is desirable when it raises image concentration that especially the degree of sphericity psi of a magnetic particle is 0.8 or more. As mean particle diameter of a magnetic particle, 0.05-1.0 micrometers is desirable still more desirable, and 0.1-0.4 micrometers is desirable.

[0047] The content of the magnetic substance in a toner is used at a rate of the 10 - 150 weight section to the binding resin 100 weight section.

[0048] As a Magenta coloring agent, a condensation azo compound, a diketo pyrrolo pyrrole compound, an anthraquinone compound, the Quinacridone compound, a base color lake compound, a naphthol compound, a bends imidazolone compound, a thioindigo compound, a perylene compound, etc. are used. The C.I. pigment red 2, 3, 5, 6, 7, and 23, 48:2, 48:3, 48:4, 57:1, 81:1, and 122, 146, 166, 169, 177, 184, 185, 202, 206 and 220,221,238,254 are especially specifically desirable. these are independent -- or two or more sorts can use it, mixing.

[0049] It is desirable as a coloring agent of this invention especially from the field of a development property when the C.I. pigment red 122 or the C.I. pigment red 238 considers as a toner. These blending ratio of coal is 1 - 5% of the weight of range.

[0050] Furthermore, it is desirable from a development property to contain the C.I. pigment red 122 and the C.I. pigment red 238 in coincidence, and it is more desirable to contain in 1 - 4% of the weight of the range, respectively.

[0051] As a cyanogen coloring agent used for this invention, a copper-phthalocyanine compound and its derivative, an anthraquinone compound, a base color lake compound, etc. can be used. concrete -- the C.I. pigment blues 1, 7, and 15, 15:1, and 15: -- 2, 2, 15:3, 15:4, 60 and 62, and 66 grades are mentioned, and it can use suitably especially. these are independent -- or two or more sorts can be mixed and it can be further used in the state of the solid solution. Especially, it is desirable from development specially made to contain a copper-phthalocyanine pigment one to 5% of the weight.

[0052] As a yellow coloring agent used for this invention, the compound represented by a condensation azo compound, an isoindolinone compound, the Anthraquinone compound, an azo metal complex, a methine compound, and the allyl compound amide compound is used. the C.I. pigment yellow 12, 13, 14, 15, 17, 62, 74, 83, 93, 94, 95, 109, 110, 111, and 128 and 129,147,168,180 grades are mentioned, and, specifically, these are independent -- or two or more sorts can use it, mixing. It is desirable from the field of a development property to contain the C.I. pigment yellow 17, the C.I. pigment yellow 74, or the C.I. pigment yellow 180 one to 5% of the weight especially.

[0053] The above-mentioned coloring agent is chosen from the point of a hue angle, saturation, lightness, weatherability, OHP transparency, and the dispersibility to the inside of a toner. Moreover, the blending ratio of coal of this coloring agent is 1 - 10 weight section to the resin 100 weight section.

[0054] Moreover, it is desirable to set to the toner of this invention and to also make the following waxes contain in a toner particle from the point of the improvement of the mold-release characteristic from the fixing member at the time of fixing in improvement fixable.

[0055] A polyolefine wax and its derivative, a polypropylene wax and its derivative, polyethylene wax and its derivative, paraffin wax and its derivative, a micro crystallin wax and its derivative, the Fischer Tropsch wax and its derivative, ester wax and its derivative, carnauba wax and its derivative, other natural waxes, its derivative, etc. are mentioned. Oxide, and a block copolymer with a vinyl system monomer and a graft denaturation object are included in a derivative.

[0056] When the Fischer Tropsch wax, paraffin wax, ester wax, higher alcohol, etc. are used for the nonmagnetic 1 component developing-negatives method with which the coat of the toner is carried out by the blade on a development sleeve, and the development of an electrostatic-charge image is presented also in these, it is desirable from the field of a development property.

[0057] as the example of the above-mentioned wax -- for example, carnauba wax, a candelilla wax, jojoba oil, hydrogenation jojoba oil, a rice wax, a montanoic acid wax, the LUVAX series by NIPPON SEIRO CO., LTD., HNP series, and Mitsuhiro -- formation -- shrine Sun Wacks series and the Mitsui Chemicals, Inc. make -- yes, wax series, the Para Flint series made from Schumann SAZORU, H1 and H2, the Clariant, LTD. make H4, R21 grade, the uni-phosphorus series by the PETORO light company, etc. are mentioned.

[0058] As a wax, the thing within the limits the range whose on-set temperature is 50-120 degrees C, and whose peak temperature are 60-140 degrees C is desirable in the DSC curve measured with a differential scanning calorimeter. In measurement of a DSC curve, it measured by DSC made from SEIKO Electron.

[0059] The blending ratio of coal of the wax in this invention can be contained in 1 - 10% of the weight of the range.

[0060] As other additives, silicone oil, alcohol, a fatty acid, an acid amide, ester, a ketone, hydrogenated castor oil and its derivative, a vegetable system wax, an animal system wax, a mineral system wax, a PETORO lactam, etc. can be used.

[0061] Furthermore, it is desirable to make an electric charge control agent contain in the toner particle of this invention. There is the following matter to control a toner to negative electric charge nature. For example, an organometallic compound and a chelate compound are effective and there are metallic compounds of monoazo metallic compounds, acetylacetone metallic compounds, an aromatic series hide ROKISHI carboxylic acid, and an aromatic series die carboxylic-acid system. There are other phenol derivatives, such as an aromatic series hide ROKISHI carboxylic acid, aromatic series monochrome, polycarboxylic acid and its metal salt, an anhydride, ester, and a bisphenol. Moreover, a urea derivative, a metal-containing salicylic-acid system compound, a metal-containing naphthoic-acid system compound, a boron compound, quarternary ammonium salt, carixarene, a silicon compound, a styrene-acrylic-acid copolymer, a styrene-methacrylic-acid copolymer, a styrene-acrylic-sulfonic-acid copolymer, a non metal carboxylic-acid system compound, etc. are mentioned. Especially, the metallic compounds, the boron complex compound, or annular phenol system oligomer of a field to a salicylic acid of electrification nature and a tint is desirable, and carixarenes are mentioned as the boron complex compounds of alpha-hydroxycarboxylic acid, and annular phenol system oligomer as a boron complex compound.

[0062] As an example of these compounds, BONTORON E81, BONTORON E84, BONTORON E88 (the ORIENT chemistry incorporated company make, trade name) and TN105 (the Hodogaya chemistry incorporated company make, trade name), etc. are mentioned as metallic compounds of a salicylic acid. As for these, it is desirable to contain 0.5 to 10% of the weight in a toner.

[0063] It is desirable for LR147 (the Japan Carlit Co., Ltd. make, trade name) to be mentioned, and to contain 0.5 to 3% of the weight in a toner as an example of a boron complex compound, for example.
[0064] It is desirable for BONTORON E89 (the ORIENT chemistry incorporated company make, trade name) to be mentioned, and to contain 0.5 to 2% of the weight in a toner as an example of annular phenol system oligomer, for example.
[0065] as a particle of the electric charge controllability **(ed) outside in this invention, metallic oxides (tin oxide, titanium oxide, a zinc oxide, silicon oxide, aluminum oxide, etc.), carbon black, etc. are mentioned, and these are independent -- or two or more sorts can use it, mixing.
[0066] the blending ratio of coal of the above-mentioned external additive -- the toner particle 100 weight section -- receiving -- 0.1 - 10 weight section -- it is 0.1 - 5 weight section preferably.
[0067] The content of 5.8-10.5 micrometers and 5.0 micrometers or less contains [a weight mean diameter] the toner of this invention 20% or less with the number, and it is desirable that the content of 20 micrometers or more is 1.0% or less by weight. It comes out and a certain thing is desirable. The content of 5.0 micrometers or less is 16% or less with the number more preferably.
[0068] Measurement of this grain size was performed by the following approaches the Coulter counter method. Although the electrolytic solution prepares a NaCl water solution 1% using the 1st class sodium chloride using a coal tar multi-sizer (coal tar company make), it is ISOTON as the electrolytic solution. R-11 (made in coal tar scientific Japan) can be used. As a measuring method, 0.1-5ml of alkylbenzene sulfonate is added as a dispersant into 100-150ml of said electrolysis water solutions, and 2-20mg of test portions is added. The electrolytic solution which suspended the sample performed distributed processing for about 1 minute with the ultrasonic distribution vessel, measured the volume of a toner 2.05 micrometers or more, and the number in 100-micrometer aperture and the 256-channel mode with said measuring device, and computed gravimetric analysis and number distribution.
[0069] What metallic oxides (silicon oxide, an aluminum oxide, titanium oxide, etc.), carbon black, fluoride carbon, a silica, etc. were mentioned, and performed hydrophobing processing, respectively as a flow grant agent **(ed) outside by the toner particle used for this invention is desirable. Especially, it is good to use pulverized coal with a particle size [of a silica (SiO2)] of 0.001-20 micrometers, and the thing which carried out hydrophobing of the front face of the thing of 0.01-1.0-micrometer pulverized coal by the silane coupling agent, silicone oil, etc. especially. As for silica pulverized coal, it is desirable to be contained in the range of the 0.1 - 4.0 weight section to the toner particle 100 weight section. When fewer than the 0.1 weight section, a fluidity cannot be enough given to a toner particle but the concentration on an image may become low. When [than the 4.0 weight sections] more, photo conductor welding and the amount of electrifications under low temperature and damp increase, the fall of image concentration is imitated, and it is **.
[0070] as an abrasive material **(ed) outside in this invention, a metallic oxide, nitrides (strontium titanate, cerium oxide, an aluminum oxide, a magnesium oxide, chrome oxide, etc.) (silicon nitride etc.), carbide, metal salts (silicon carbide etc.) (a calcium sulfate, a barium sulfate, calcium carbonate, etc.), etc. are mentioned, and these are independent -- or two or more sorts can use it, mixing.
[0071] as lubricant **(ed) outside in this invention, fluororesin powder, (vinylidene fluoride, polytetrafluoroethylene, etc. and fatty-acids) metals (zinc stearate, calcium stearate, etc.), etc. are mentioned, and these are independent -- or two or more sorts can use it, mixing.
[0072] The manufacture approach of the grinding toner of this invention The pigment or color as binding resin, the low softening temperature matter, and a coloring agent, An electric charge control agent and other additives are fully mixed with a Henschel mixer and a mixer like a ball mill if needed. Melting kneading of the obtained mixture is carried out using a heating roller, a kneader, and a heat kneading machine like an extruder. The low softening temperature matter, a pigment, a color, and the magnetic substance are made to be able to distribute or dissolve in the inside in which the resinous principle of each other was dissolved, grinding after cooling solidification and a classification can be performed for the obtained kneading object, and a toner can be obtained. Furthermore, the toner which adds an external additive and is applied to this invention behind mixing and a screen cliff with a mixer like a Henschel mixer can be obtained.

[0073] in using the toner of this invention as a binary system developer, it mixes with a carrier, is used and uses the mixing ratio of a toner and a carrier by 0.1 - 50 mass % as toner concentration -- having -- desirable -- 0.5 to 20 mass % -- it is three to 10 mass % more preferably.
[0074] As these carrier core materials, the metals of the iron which is not oxidized [scaling or], cobalt, nickel copper, zinc, manganese, and chromium rare earth, those alloys, a compound, an oxide, a magnetic ferrite, etc. are used, for example. What contains a ferrite carrier more than 98 mass % especially is used preferably. There is no special constraint as the manufacture approach of a carrier. Especially the coat carrier that covered the front face of core material with resin etc. is desirable. As an approach of covering, cladding materials, such as resin, are made to dissolve or suspend in a solvent, covering liquid is prepared, and well-known approaches, such as an approach of applying this covering liquid to a carrier particle front face, and making it adhering to a carrier particle front face, and the approach of only blending dryly a carrier particle and covering fine particles, can be applied conventionally.
[0075] As binding resin used for covering of a coat carrier Styrene, such as styrene and KURORU styrene; Ethylene, a propylene, Monoolefins, such as a butylene and an isobutylene; Vinyl acetate, propionic-acid vinyl, Vinyl ester, such as benzoic-acid vinyl and butanoic acid vinyl; A methyl acrylate, An ethyl acrylate, butyl acrylate, acrylic-acid dodecyl, acrylic-acid octyl, Acrylic-acid phenyl, a methyl methacrylate, ethyl methacrylate, methacrylic-acid butyl, alpha-methylene aliphatic series monocarboxylic acid ester, such as methacrylic-acid dodecyl; Vinyl methyl ether, Vinyl ether, such as vinyl ethyl ether and vinyl butyl ether; the homopolymer of vinyl ketones, such as a vinyl methyl ketone, vinyl hexyl RUKETON, and a vinyl isopropenyl ketone, or a copolymer is mentioned. As typical binding resin, a polystyrene and styrene-acrylic-acid alkyl copolymer, a styrene acrylonitrile copolymer, a styrene-butadiene copolymer, a styrene maleic anhydride copolymer, polyethylene, polypropylene, etc. are especially mentioned from the point of the dispersibility of a conductive particle, the paint film nature as a coat layer, toner SUPENTO prevention, and productivity etc. Furthermore, a polycarbonate, phenol resin, polyester, a polyurethane epoxy resin, polyolefine, a fluororesin, silicone resin, a polyamide, etc. are mentioned. It is more desirable to include resin with small critical surface tension, for example, polyolefine, a fluororesin, silicone resin, etc. from a viewpoint of SUPENTO prevention especially.
[0076] In addition, 1.0 - 60 mass % is suitable for the amount of blends, and its 2.0 - 40 mass % is [the rate of the fluororesin or the polyolefine system tree to the total amount of binders, or silicone system resin] especially desirable. The surface treatment effectiveness is not enough in a content being under 1.0 mass %, and there is no effectiveness in toner SUPENTO. Moreover, since both cannot be easily distributed by homogeneity if 60 mass % is exceeded, it is because partial nonuniformity arises in a volume-resistivity value and an electrification property worsens.
[0077] In addition, as a fluororesin used as binding resin for covering of a carrier, the copolymer of the solvent fusibility of vinyl fluoride, vinylidene fluoride, trifluoro ethylene, chlorotrifluoroethylene, dichlorodifluoroethene, tetrafluoroethylene, hexafluoropropylene, etc. and other monomers is mentioned, for example. moreover, as silicone resin used as binding resin for covering of a carrier For example, Shin-etsu silicone company make, KR271, KR282, KR311, KR255, KR155 (straight silicone varnish), KR211, KR212, KR216, KR213, KR217, KR9218 (silicone varnish for denaturation), SA-4, KR206, KR5206 (silicone alkyd varnish), ES1001, ES1001N, ES1002T, ES1004 (silicone epoxy varnish), KR9706 (silicone acrylic varnish), KR5203, KR5221 (Silicone polyester varnish) SR2100, SR2101, SR2107, SR2110, SR2108, SR2109, SR2400, SR2410, SR2411 and SH805 by the Toray Industries silicone company, SH806A, and SH840 grade are used.
[0078] although what is necessary is just to determine the amount of the above-mentioned ingredient used suitably -- general -- a total amount -- a carrier -- receiving -- 0.1 to 30 mass % -- 0.5 - 20 mass % is preferably desirable.
[0079] As for the mean particle diameter of a carrier, it is more preferably desirable preferably that it is 25-65 micrometers 25-70 micrometers 20-100 micrometers.
[0080] Especially, as a desirable carrier, it is 3 element ferrite particle of Cu-Zn-Fe [presentation weight

ratio (5-20):(5-20): (30-80)], and what covered the front face with fluorine ******, styrene resin, silicone resin, or those mixed resin is mentioned. as for example, mixed resin -- polyvinylidene fluoride, styrene-methylmetaacrylate resin; polytetrafluoroethylene, styrene-methylmetaacrylate resin; fluorine system copolymer, and styrene system copolymer; etc. -- 90:10-20:80 -- the mixture of the weight ratio of 70:30-30:70 is mentioned preferably. 0.01 to 5 mass % and the coat magnetism ferrite carrier with which it is made desirable 0.1-1 mass % coating, 250 meshes are passed, and an ON ** carrier particle has a certain above-mentioned mean particle diameter more than 70 mass % in 350 meshes are mentioned as a desirable carrier in a coating agent. As this fluorine system copolymer, a vinylidene fluoride-tetrafluoroethylene copolymer (10:90-90:10) is illustrated and a styrene-2-ethylhexyl acrylate copolymer (20:80-80:20) and a styrene-acrylic-acid 2-ethyl hexyne-methyl-methacrylate copolymer (20-60:5-30:10-50) are illustrated as a styrene system copolymer.

[0081] To the toner of this invention, the sharp above-mentioned coat magnetism ferrite carrier of particle size distribution gives desirable frictional electrification, and is effective in raising electrophotographic properties further.

[0082] the case where mix the toner and carrier of this invention and a two component developer is prepared -- the mixing ratio -- a rate -- as the toner concentration in a developer -- 1 mass % - 15 mass % -- if it is preferably made 2 mass % - 13 mass %, a usually good result will be born. When image concentration becomes low and exceeds 15 mass %, it makes fogging and scattering inside the plane increase under by 1 mass %, and toner concentration tends to shorten the useful life longevity of a developer.

[0083] When using nonmagnetic monocomponent toner, using a blade or a roller, frictional electrification of the toner of this invention is compulsorily carried out with a development sleeve, and it usually has the approach of making it convey by making a toner adhere on a sleeve.

[0084] The conceptual diagram of the developer used for the nonmagnetic 1 component development approach of this invention in this invention at drawing 1 is shown. The development counter with which 1 holds a toner, and 2 are photo conductors which rotate in the direction of a. The photo conductor 2 of a development counter 1 is equipped with the development sleeve 11 in the part by which opposite arrangement is carried out, and the development sleeve 11 develops the electrostatic image on a photo conductor 2, and uses it as a toner image while it supports a toner. Even if the development sleeve 11 and the photo conductor 2 which counters prepare very small spacing, it may be contacted and the development sleeve 11 makes the forward direction rotate it to the hand of cut of a photo conductor 2. In addition, the development sleeve 11 may carry out the gestalt of not only the thing of the shape of a cylinder as shown in drawing but the endless belt which carries out a rotation drive, and a conductive rubber roller may be used for it.

[0085] Furthermore, as elastic specification-part material, the elastic blade 12 is formed in a development counter 1, and the toner spreading roller 13 is formed in the upper part location of the development sleeve 11 rather than the elastic blade 12 in the location by the side of the improvement style in the method of rotation of the development sleeve 11 at it. In addition, an elastic roller may be formed as elastic specification-part material. The elastic blade 12 is inclined and formed in the sense which falls towards the improvement style side in the method of rotation of the development sleeve 11, counters and is contacted by the up peripheral face of the development sleeve 11 in a hand of cut. In addition, 14 is the impeller of the toner held in the development counter 1.

[0086] The resin blade of the product [thing / which was stuck] made of the product made from urethane or silicone rubber is sufficient as the resin chip of the product [blade / 12 / elastic / metal /, such as copper, iron, and stainless steel, / contact area / with the development sleeve 11 on a metal blade] made of the product made from urethane, or silicone rubber.

[0087] The conductive cylinder in which the development sleeve 11 was formed with the metal or alloy like aluminum and stainless steel is used preferably. The conductive cylinder could be formed with the resin constituent which has a sufficient mechanical strength and conductivity. Furthermore, the development sleeve 11 may have the enveloping layer by which the conductive particle is distributed by the cylindrical surface made from metal or an alloy. Into an enveloping layer, as for an enveloping layer, that in which the mixture of a carbon particle, a carbon particle, and crystalline graphite or a crystalline graphite conductivity particle is contained is used, using acrylic resin or phenol resin as a resin ingredient.

[0088] To the development sleeve 11, it is contacted by a photo conductor 2 and the opposite side, and the toner spreading roller 13 is supported pivotable.

[0089] The contact section of the elastic blade 12 and the development sleeve 11 is passed, the foil layer of a toner is formed on the development sleeve 11, and the toner supplied with the spreading roller 13 is conveyed to a photo conductor 2 and the development part which has countered. By impressing the mutual electrical potential difference which superimposed the alternating current to a direct current with a bias impression means as development bias, the toner on the development sleeve 11 transfers to the development sleeve 11 corresponding to the electrostatic-charge image formed on the photo conductor 2, and adhesion and a toner image are formed in it at an electrostatic-charge image.

[0090]

[Example] Although an example explains this invention concretely below, this invention is not limited at all by the following examples. In addition, the "section" means the "weight section."

[0091] The pigment and polyester resin of the [example 1 of manufacture of masterbatch] following were put into the kneader, and it kneaded for 30 minutes after heating at 100 degrees C. The speed mill which made the kneading object tabular and attached a mesh with a diameter of 2mm after cooling ground, and the resin constituent R1 was obtained.

[0092]

- Polyester resin (a bisphenol A propyl oxide 2mol addition product, the copolymer of a fumaric acid, molecular weight: 24300, Mw/Mn:5.5, acid-number:10.3 mgKOH/g) 60 sections and the C.I. pigment 122 20 sections and C.I. pigment 238 The resin constituent R2 was obtained like the example 1 of manufacture using the pigment and polyester resin of the 20 sections [example 2 of manufacture of masterbatch] following.

[0093]

- Polyester resin (a bisphenol A propyl oxide 2mol addition product, the copolymer of a fumaric acid, molecular weight: 21600, Mw/Mn:4.2, acid-number:9.1 mgKOH/g) 60 sections and C.I. pigment 238 The resin constituent B1 was obtained like the example 1 of manufacture using the pigment and polyester resin of the 40 sections [example 3 of manufacture of masterbatch] following.

[0094]

- Polyester resin (a bisphenol A propyl oxide 2mol addition product, the copolymer of a fumaric acid, molecular weight: 24300, Mw/Mn:5.5, acid-number:10.3 mgKOH/g) 60 sections and C.I. pigment blue 15:3 The resin constituent Y1 was obtained like the example 1 of manufacture using the pigment and polyester resin of the 40 sections [example 4 of manufacture of masterbatch] following.

[0095]

- Polyester resin (a bisphenol A propyl oxide 2mol addition product, the copolymer of a fumaric acid, molecular weight: 24300, Mw/Mn:5.5, acid-number:10.3 mgKOH/g) 60 sections and C.I. pigment yellow 17 The resin constituent R3 was obtained like the example 1 of manufacture using the pigment and polyester resin of the 40 sections [example 5 of manufacture of masterbatch] following.

[0096]

- Polyester resin (the copolymer of ethylene glycol, propylene glycol, and terephthalic acid, molecular weight 32000, Mw/Mn7.0, acid-number 5.8 mgKOH/g) 60 sections and C.I. pigment 238 The 40 sections [the example 1 of manufacture of binding resin]
- Terephthalic acid 6.0 mol and isophthalic acid 3.0mol and bisphenol A propylene oxide 2.2mol addition product 7.0 mol and ethylene glycol 2.0 mol and a diethylene glycol 1.0 mol and Djibouti rutin oxide After putting the 0.05g above-mentioned compound into a reactor, attaching a thermometer, a stirring rod, a capacitor, and nitrogen installation tubing and carrying out a nitrogen purge, a temperature up is carried out gradually, stirring, and subsequently to 190 degrees C the temperature up was carried out, and it was made to make it react for 5 hours and to react at 170 degrees C, for 4 hours. Then, the following compounds were added.

[0097]
- Trimellitic anhydride 0.9 mol and Djibouti rutin oxide After that [0.3g], made it react at 190 degrees C for 3 hours, carry out a temperature up to 200 more degrees C, decompress (10hPa), and it was made to react for 4 hours, and dehydration condensation was carried out, the reaction was ended, and polyester resin A was obtained. Weight-average-molecular-weight Mw:115000, Mw/Mn:39.8, P1:6700, and with a molecular weight of 150000 or more component:15.1%, P2: did not exist but obtained polyester resin A was acid-number:4.0 mgKOH/g, OH **:9.5, and Tg:62.3 degree C.
[0098]
[The example 2 of manufacture of binding resin]
- Terephthalic acid 6.0 mol and isophthalic acid 3.0 mol and ethylene glycol 6.0 mol and ethanol 8.0 mol and Djibouti rutin oxide After putting the 0.05g above-mentioned compound into a reactor, attaching a thermometer, a stirring rod, a capacitor, and nitrogen installation tubing and carrying out a nitrogen purge, a temperature up is carried out gradually, stirring, and subsequently to 190 degrees C the temperature up was carried out, and it was made to make it react for 5 hours and to react at 170 degrees C, for 4 hours. Then, the following compounds were added.
[0099]
- Bisphenol A propylene oxide 2.2mol addition product 7.0 mol and ethylene glycol 1.0 mol and a diethylene glycol 2.0 mol and a glycerol 0.3 mol and Djibouti rutin oxide after that [0.5g], it is made to react at 190 degrees C for 3 hours, and a temperature up is carried out to 200 more degrees C, and it decompresses (10hPa), and reacts for 4 hours -- making -- an ester exchange reaction -- dehydration condensation was carried out, the reaction was ended and polyester resin B was obtained. obtained polyester resin B -- weight-average-molecular-weight Mw:99000 and Mw/Mn: -- they were P 2:134**, acid-number:0.6 mgKOH/g, OH **:14, and Tg:63.0 degree C 31.7, P1:7400, and with a molecular weight of 150000 or more component:13.2%.
[0100]
[The example 3 of manufacture of binding resin]
- Terephthalic acid 6.0 mol and isophthalic acid 3.0mol and bisphenol A ethyleneoxide 2.3mol addition product 7.0 mol and ethylene glycol 2.0 mol and a diethylene glycol 2.0 mol and Djibouti rutin oxide After putting the 0.05g above-mentioned compound into a reactor, attaching a thermometer, a stirring rod, a capacitor, and nitrogen installation tubing and carrying out a nitrogen purge, a temperature up is carried out gradually, stirring, and subsequently to 200 degrees C the temperature up was carried out, and it was made to make it react for 5 hours and to react at 170 degrees C, for 4 hours. Then, the following compounds were added.
[0101]
- Trimellitic anhydride 2.4 mol and Djibouti rutin oxide After that [0.7g], made it react at 200 degrees C for 3 hours, carry out a temperature up to 230 more degrees C, decompress (10hPa), and it was made to react for 4 hours, and dehydration condensation was carried out, the reaction was ended, and polyester resin C was obtained. obtained polyester resin C -- weight-average-molecular-weight Mw:562000 and Mw/Mn: -- they were P 2:1000**, acid-number:18.4 mgKOH/g, OH **:21.5, and Tg:56.2 degree C 55.4, P1:9600, and with a molecular weight of 150000 or more component:35.1%.
[0102]
Example 1 and polyester resin A 85 sections and the resin constituent R1 10 sections and a screw-(diphenyl oxo-acetyl) boron potassium 3 sections and the Fischer Tropsch wax (the product made from Schumann SAZORU, Para Flint H1) After carrying out mixed distribution of the 2 section above-mentioned configuration raw material with a Henschel mixer (Mitsui Mining Co., Ltd. make), the 2 shaft kneading machine (PCM30 by IKEGAI CORP.) performed melting kneading, and coarse grinding was further carried out with the speed mill. The coarse-grinding object pulverized and classified with the IDS-2 mold grinder (Japanese pneumatic company make) and the DSX-2 mold classifier (Japanese pneumatic company make), and the toner classification article (M powder) was obtained.
[0103] The toner was obtained having ******(ed) the 1.5 sections and a hydrophobing processing titanium oxide compound outside with 0.5 ****** and a Henschel mixer (above), and having applied

the hexamethyldisilazane treatment hydrophobic silica to the ultrasonic vibration screen (product made from the Dalton stock) further to this toner classification article (M powder) 100 section.

[0104] When the particle size distribution of this toner classification article (M powder) was measured by the multi-sizer II (Coulter counter company make), in 9.43 micrometers and number distribution, the content with a particle diameter of 5 micrometers or less was [in / in the weight mean diameter of a toner / the volume integral cloth / content with a particle diameter of 20 micrometers or more] 0.0% several 14.0%.

[0105] This toner was applied to the printer and cartridge which converted TF6500 (the Toshiba TEC Corp. make, trade name) of regular paper facsimile, and image formation was performed. The photo conductor made the toner negative electrification nature using the negative electrification nature organic photo conductor drum, the developing roller used the phenol resin which a carbon particle and conductive graphite contained as aluminum tubing by which the coat was carried out to the front face, and the blade was made into the metallic thin plate which stuck urethane resin on the contact section with a developing roller. It was made into 280 micrometers between the front face of an organic photo conductor drum, and the developing-roller front face. The toner spreading roller was used as the sponge roller on which the urethane containing a conductive agent was made to foam.

[0106] [Image evaluation trial] A4 image was outputted after leaving this reconstruction printer under ordinary temperature and normal relative humidity (23 degrees C, 60%RH), and image evaluation was performed. The good image was obtained when a poor image, an alphabetic character image, and white were outputted. After outputting 2000 images of the poor **** alphabetic character of 5 moremm angle, when a poor image, an alphabetic character image, and white were outputted, the good image without fogging was obtained. The evaluation result was collectively shown in Table 1. Fogging evaluation, O:A, O**:good, **:good, **x:improper, x: **.

[0107] The blank paper was stuck on the [toner scattering evaluation] developing-roller lower part, and viewing estimated the dirt of the part. O : A, O**:good, **:good, **x:improper, x:**.

[0108] On a [gradation nature evaluation] photo conductor, the printing pixel ratio per unit area forms the latent image of four steps of halftone images (including ****), 100%, 75%, 50%, and 25%, and develops and carries out image formation of this. This concentration was measured and gradation nature was evaluated.

[0109] After leaving this reconstruction printer for two days under low temperature and a damp environment (15 degrees C, 10%RH) in an elevated temperature and a high-humidity environment (30-degree-C, 80%RH) list, similarly image evaluation was performed to an elevated temperature, a high-humidity environment, low temperature, and a [damp environmental-test] pan. The evaluation result summarized the result in an elevated temperature and a high-humidity environment (30 degrees C, 80% RH) in Table 2, and summarized the result under low temperature and a damp environment (10 degrees C, 20%RH) in Table 3.

[0110] [Fixing sex test] The fixable trial was performed using 64g paper, making the skin temperature of a fixing assembly change from 120 degrees C to 230 degrees C using this printer. Fixing initiation temperature and offset generating temperature were searched for, and the result was summarized in Table 4.

[0111]

Example 2 and polyester resin A 85 sections and resin constituent B1 10 sections and JI t-butyl salicylic-acid zinc compound 3 sections and the Fischer Tropsch wax (the NIPPON SEIRO CO., LTD. make, MDP7010)

The toner was manufactured like the example 1 except changing the charge of 2 members above. It was similarly estimated as the example 1 and the obtained result was summarized in Table 4 from Table 1.

[0112]

Example 3 and polyester resin A 85 sections and resin constituent Y1 10 sections and screw-(diphenyl oxo-acetyl) boron potassium 3 sections and higher alcohol (PETORO light company make, uni-phosphorus 350) The toner was manufactured like the example 1 except changing the charge of 2 members above. It was similarly estimated as the example 1 and the obtained result was summarized in

Table 4 from Table 1.

[0113]

Example 4 and polyester resin B 85 sections and the resin constituent R1 10 sections and a screw-(diphenyl oxo-acetyl) boron potassium 3 sections and the Fischer Tropsch wax (the product made from Schumann SAZORU, Para Flint H1) The toner was manufactured like the example 1 except changing the charge of 2 members above. It was similarly estimated as the example 1 and the obtained result was summarized in Table 4 from Table 1.

[0114]

Example 5 and polyester resin B 85 sections and the resin constituent R2 10 sections and a JI t-butyl salicylic-acid zinc compound 3 sections and the Fischer Tropsch wax (the product made from Schumann SAZORU, Para Flint H1) The toner was manufactured like the example 1 except changing the charge of 2 members above. It was similarly estimated as the example 1 and the obtained result was summarized in Table 4 from Table 1.

[0115]

Example 6 and polyester resin B 85 sections and the resin constituent R3 10 sections and a JI t-butyl salicylic-acid zinc compound 3 sections and the Fischer Tropsch wax (the product made from Schumann SAZORU, Para Flint H1) The toner was manufactured like the example 1 except changing the charge of 2 members above. It was similarly estimated as the example 1 and the obtained result was summarized in Table 4 from Table 1.

[0116]

Example 7 and polyester resin C 85 sections and resin constituent R1 10 sections and p-t-butyl calyx [8] arene compound 2 sections and petroleum wax LUVAX1121 (NIPPON SEIRO CO., LTD. make) The toner was manufactured like the example 1 except changing the charge of 2 members above. It was similarly estimated as the example 1 and the obtained result was summarized in Table 4 from Table 1.

[0117]

Example of comparison 1, and polyester resin C 85 sections and resin constituent R3 10 sections and sulfonic group content styrene acrylic polymer 3 section and screw call 660P (Mitsuhiro formation shrine make) The toner was manufactured like the example 1 except changing the charge of 2 members above. It was similarly estimated as the example 1 and the obtained result was summarized in Table 4 from Table 1.

[0118]

[Table 1]

例 / 特性	実施例							比較例
	1	2	3	4	5	6	7	1
初期画像								
階調濃度								
100%	1.45	1.65	1.52	1.43	1.40	1.32	1.36	1.25
70%	0.97	0.86	0.99	0.86	0.77	0.68	0.73	0.67
50%	0.53	0.46	0.49	0.49	0.48	0.42	0.43	0.40
25%	0.21	0.15	0.20	0.20	0.17	0.17	0.17	0.14
カブリ	○	○	○	○	○	○	○	○△
2000枚後画像								
階調濃度								
100%	1.43	1.65	1.47	1.41	1.39	1.30	1.25	1.19
70%	0.98	0.95	1.03	0.95	0.75	0.69	0.67	0.60
50%	0.52	0.48	0.59	0.50	0.41	0.38	0.37	0.33
25%	0.20	0.18	0.18	0.20	0.17	0.14	0.15	0.13
カブリ	○	○	○	○	○△	○△	○△	△
転写効率	86	85	84	81	80	78	77	72
トナー飛び散り	○	○	○	○	○	○△	○△	△×

[Table 2]

例 / 特性	実施例							比較例
	1	2	3	4	5	6	7	1
初期画像								
濃度	1.46	1.65	1.52	1.45	1.43	1.33	1.37	1.27
カブリ	○	○	○	○△	○△	○△	△	△
1000枚後画像								
濃度	1.44	1.62	1.51	1.44	1.40	1.31	1.30	1.22
カブリ	○	○	○	○△	△	△	△	△×
転写効率	83	81	81	76	76	73	70	65
トナー飛び散り	○	○	○	○△	○△	△	△	△×

[Table 3]

例 特性	実施例							比較例
	1	2	3	4	5	6	7	1
初期画像								
濃度	1.42	1.58	1.45	1.35	1.33	1.25	1.26	1.19
カブリ	○	○	○	○	○△	○△	○△	○△
1000枚後画像								
濃度	1.44	1.65	1.45	1.40	1.39	1.33	1.26	1.20
カブリ	○	○	○	○	○	○	○	○△
転写効率	82	79	84	83	83	77	75	67
トナー飛び散り	○	○	○	○△	○△	○△	○△	○△

[Table 4]

例 特性	実施例							比較例
	1	2	3	4	5	6	7	1
定着開始温度（℃）	130	130	130	130	130	130	140	150
オフセット発生温度（℃）	230	230	230	230	230	220	230	230

[0119]
[Effect of the Invention] As explained above, according to the toner of this invention, the toner which gives the image quality for which imprint effectiveness is high, there is no fogging, and it does not depend on an environment by high definition can be obtained.

[0120] Moreover, while having the outstanding imprint property, color enhancement is high, the image quality concentration of the poor section to halftone is also high, and the toner which was excellent in stability in addition can be obtained.

[0121] Furthermore, there is little spilling from a development sleeve and the toner which mitigates the printer which forms an image, and the dirt by toner scattering inside a copying machine can be obtained.

[Translation done.]